Rohrer, Duax & Fullerton (1976) as the two energetically favored orientations for the *E* ring.

The hydrogen bonds* form an extensive network stabilizing the structure, as shown in Fig. 4. The solvent molecule, presumably a disordered methanol, has its O in two positions, (1) and (2). In position (1), this O is at hydrogen-bonding distance to hydroxyl O(14) and also to O(19) of the adjacent molecule, while in position (2) this O is capable of hydrogen bonding with O(3).

It appears that in spite of the additional sugar unit, the aglycone portion of ouabain shows little conformational change from that of ouabagenin; hence the irreversible inhibition of ouabain may be associated with the binding of the sugar moiety, as postulated earlier (Yoda, 1973; Wallick *et al.*, 1974).

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* See deposition footnote.

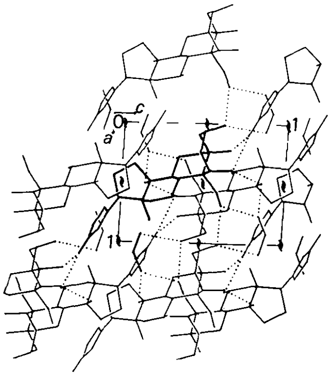

Fig. 4. Packing of molecules in the unit cell (viewed down **b**) with H bonding indicated by dotted lines.

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Tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene-11,11-dicarbonitrile, $C_{13}H_8N_2$, at 150 K

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Abstract. $M_r = 192\cdot2$, orthorhombic, space group $P2_12_12_1$, $a = 5\cdot969\,(2)$, $b = 10\cdot370\,(3)$, $c = 15\cdot546\,(5)$ Å, $V = 962\cdot3\,(5)$ Å^3, $Z = 4$, $D_m = 1\cdot280\,(5)$, $D_x = 1\cdot327$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot075$ mm^{-1}, $F(000) = 400$. Final $R = 0\cdot048$ based on 2307 observed independent reflections. The X-ray study of the title compound has shown the presence of the cyclopropane ring with normal bond lengths. The alternation of single and double bonds along the annulene perimeter confirms the bis-8,9,10-trinorcaradienic character of the molecule.

Introduction. The equilibrium [10]annulene ⇄ bis-8,9,10-trinorcaradiene has attracted the interest of organic chemists for many years (Vogel, 1967, 1969) and has been extensively studied by X-ray diffraction in our laboratory. On going from (1) to (2) a large variation in the C(1)—C(6) distance is involved. Reported values for this distance are 2·269 (5) Å ($R = R' = \text{F}$, 1*a*) (Pilati & Simonetta, 1976), 2·235 (3) Å ($R = R' = \text{H}$, 1*b*) (Bianchi, Pilati & Simonetta, 1980), 1·771 (8), 1·827 (8) Å ($R = R' = \text{CH}_3$, 2*b*) (Bianchi, Morosi, Mugnoli & Simonetta, 1973), and 1·640–1·851 Å ($R = \text{CH}_3$, $R' = \text{CN}$, 2*c*) Bianchi, Pilati & Simonetta, 1978, 1981). The title compound ($R = R' = \text{CN}$, 2*a*) has been recently synthesized (Vogel, Scholl, Lex & Hohlneicher, 1982) and NMR results suggested the form (2) with a strong C(1)—C(6) bond (Günther & Schmickler, 1974). So, the crystal structure has been determined to check its polyenic character. To

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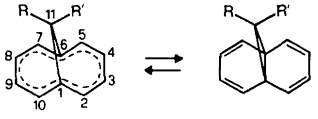
reduce the effect of thermal motion, data were collected at 150 K.



(1) (2)

Experimental. D_m measured at room temperature by flotation in dilute K_2HgI_4, spherical crystal, radius 0·14 mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, 3363 *hkl* with $2\theta < 80°$, Lp correction, absorption ignored; direct methods (*MULTAN*, Germain, Main & Woolfson, 1971), 2307 observed with $I > 3\sigma(I)$, 202 unobserved, anisotropic full matrix, H (geometrically located) isotropic, final $R = 0{\cdot}048$, $R_w = 0{\cdot}068$, $w = 1/\sigma^2$, final secondary extinction value $g = 7{\cdot}4\,(1) \times 10^{-7}$, scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are given in Table 1.* A view of the molecule and the atomic numbering are shown in Fig. 1. A striking feature of 2(*a*) is the systematic succession of long and short bond distances along the annulene ring (see Table 2). These distances correspond to localized single and double bonds, thus indicating the polyenic character of the molecule. Another important result is the closure of the cyclopropane ring C(1), C(6) and C(11) with a C(1)–C(6) bond length of 1·539 (2) Å. So, this result represents the last stage of the 'reaction' (Bürgi, Shefter & Dunitz, 1975) sketched in the *Introduction*. Table 2 summarizes some relevant parameters of this 'reaction'. The difference in C(1)–C(11) and C(6)–C(11) bond lengths [1·564 (2) and 1·573 (2) Å respectively] and the C(1)–C(6) length [1·539 (2) Å] is well accounted for by the influence of the π-electron-attracting substituents at C(11) on the Walsh orbitals of the cyclopropane ring.

The shortest intermolecular distances are $\mathrm{C}(11)\cdots\mathrm{N}(12^{\mathrm{i}}) = 3{\cdot}092\,(2)$, $\mathrm{C}(13)\cdots\mathrm{N}(12^{\mathrm{i}}) = 3{\cdot}114\,(2)$, $\mathrm{N}(13)\cdots\mathrm{H}(4^{\mathrm{ii}}) = 2{\cdot}65\,(2)$ and $\mathrm{N}(13)\cdots\mathrm{H}(7^{\mathrm{iii}}) = 2{\cdot}67\,(2)$ Å [(i) $-\frac{1}{2}+x,\ \frac{3}{2}-y,\ -z$; (ii) $\frac{3}{2}-x,\ 1-y,\ \frac{1}{2}+z$; (iii) $2-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$].

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters for the non-*H *atoms with e.s.d.'s in parentheses*

$$U_{\mathrm{eq}}(\text{Å}^2) = \tfrac{1}{6}\pi^2\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
C(1)	0·5583 (2)	0·4993 (2)	0·0559 (1)	0·0134 (2)
C(2)	0·4578 (3)	0·5016 (2)	−0·0308 (1)	0·0176 (3)
C(3)	0·5661 (3)	0·4520 (2)	−0·0992 (1)	0·0193 (4)
C(4)	0·7771 (3)	0·3846 (2)	−0·0905 (1)	0·0191 (4)
C(5)	0·8758 (3)	0·3682 (2)	−0·0133 (1)	0·0168 (3)
C(6)	0·7824 (3)	0·4273 (1)	0·0652 (1)	0·0137 (3)
C(7)	0·8237 (3)	0·3626 (2)	0·1482 (1)	0·0186 (4)
C(8)	0·6777 (4)	0·3715 (2)	0·2139 (1)	0·0224 (4)
C(9)	0·4662 (4)	0·4393 (2)	0·2045 (1)	0·0243 (4)
C(10)	0·4071 (3)	0·4958 (2)	0·1309 (1)	0·0199 (3)
C(11)	0·7790 (3)	0·5789 (1)	0·0669 (1)	0·0122 (3)
C(12)	0·8603 (3)	0·6476 (2)	−0·0070 (1)	0·0144 (3)
C(13)	0·8220 (3)	0·6435 (2)	0·1467 (1)	0·0154 (3)
N(12)	0·9278 (3)	0·7019 (2)	−0·0657 (1)	0·0228 (4)
N(13)	0·8654 (3)	0·6956 (2)	0·2098 (1)	0·0235 (3)

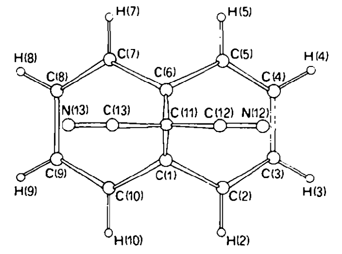


Fig. 1. A view of 2(*a*) with the numbering of atoms.

Table 2. *Relevant geometrical parameters for the 'reaction'* [10]*annulene* ⇄ *bis*-8,9,10-*trinorcaradiene*

*mm*2 symmetry is assumed for the annulene skeleton.

Parameter	2(*a*) 150 K	2(*c*) 173 K	2(*c*) Room temp.	2(*b*) Room temp., molecule *B*	2(*c*) Room temp., molecule *B*	2(*b*) Room temp., molecule *A*	2(*c*) Room temp., molecule *A*	1(*b*) Room temp.	1(*a*) 173 K
C(1)–C(6) (Å)	1·539 (2)	1·640 (1)	1·712 (2)	1·771 (8)	1·783 (3)	1·827 (8)	1·851 (3)	2·235 (3)	2·269 (5)
C(1)–C(2) (Å)	1·475 (2)	1·472 (1)	1·456 (2)	1·458 (8)	1·452 (2)	1·453 (8)	1·441 (3)	1·405 (3)	1·410 (4)
C(2)–C(3) (Å)	1·343 (2)	1·342 (1)	1·335 (3)	1·335 (8)	1·341 (3)	1·348 (8)	1·350 (3)	1·377 (4)	1·366 (4)
C(3)–C(4) (Å)	1·450 (3)	1·444 (1)	1·431 (3)	1·419 (8)	1·433 (4)	1·431 (8)	1·425 (4)	1·418 (4)	1·411 (5)
C(1)–C(11) (Å)	1·569 (2)	1·534 (1)	1·527 (2)	1·509 (8)	1·511 (3)	1·507 (8)	1·510 (3)	1·486 (3)	1·470 (4)
R–C(11)–*R'* (°)	113·6 (1)	111·8 (1)	111·0 (1)	108·9 (4)	108·9 (4)	109·5 (4)	107·6 (2)	110·6 (16)	103·0 (3)
C(1)–C(2)–C(3)–C(4) (°)	4·3 (2)	5·8 (2)	7·1 (3)	7·9 (8)	8·9 (4)	8·3 (8)	10·8 (4)	20·1 (5)	15·9 (6)
C(10)–C(1)–C(2)–C(3) (°)	151·0 (1)	145·7 (1)	144·5 (2)	140·2 (8)	144·8 (3)	139·9 (8)	144·3 (3)	145·5 (3)	139·3 (4)
σ* (Å)	0·061	0·060	0·056	0·056	0·052	0·049	0·041	0·017	0·023

* $\sigma = \langle (r_i - \bar{r})^2 \rangle^{1/2}$, where r_i are the observed bond lengths in the ring and $\bar{r} = \langle r_i \rangle$.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances, bond angles, torsion angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38235 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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11-Deoxy-7-oxa-13,14-didehydroprostaglandin E$_1$* (at 173 K), C$_{19}$H$_{30}$O$_5$

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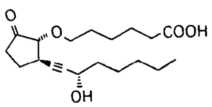
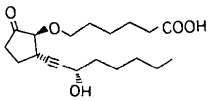
Abstract. $M_r = 338{\cdot}4$, monoclinic, $P2_1$, $a = 10{\cdot}785\ (3)$, $b = 6{\cdot}841\ (2)$, $c = 13{\cdot}176\ (4)$ Å, $\beta = 103{\cdot}05\ (2)°$, $V = 947{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}19$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}079$ mm^{-1}. Final $R = 0{\cdot}054$ for 1094 unique reflections. The molecule is virtually coplanar and possesses the 'hairpin' conformation characteristic of prostaglandin molecules. The side chains are in the fully extended all-*trans* conformation. A detailed comparison of the stereochemical features of the title compound and published prostaglandin structures is presented.

Introduction. The stereoselective syntheses of a series of 11-deoxy-7-oxa-prostaglandin analogs were recently accomplished (Matthews, Mihelich & McGowan, 1982). In the course of that work, the mixture of stereoisomers shown below was prepared. One of the two isomers crystallized and was thus obtained optically pure.



(I)



(II)

For both compounds, the absolute stereochemistry at C(15) was known to be *S* [because the synthesis started with optically pure (*S*)-1-octyn-3-ol]. The relative stereochemistry at the ring junction [C(8) *vs* C(12)] was also known to be *trans*. However, in the absence of a crystal structure, it was impossible to tell which of the two structures represented the crystalline isomer. Solution of the structure defines the molecule's stereochemistry to be (I) and allows the absolute stereochemistry of a series of compounds to be assigned through comparative chemical procedures.

Experimental. Crystals of title compound (hereinafter referred to as CE1S) obtained from Dr R. S. Matthews, crystallized by slow evaporation of a hexane solution; clear, tablet-shaped crystal, 0·03 × 0·13 × 0·55 mm, mounted on a glass fiber, transferred to a Syntex $P2_1$ autodiffractometer, data crystal continuously bathed in cold, dry nitrogen gas stream maintained at 173 K using a Syntex LT-1 low-temperature attachment, Laue symmetry $2/m$ with systematic absences $0k0$ for k odd; solution and refinement of structure confirm space group to be $P2_1$, lattice parameters obtained by least-squares analysis of 14 carefully centered reflections, $hk\pm l$ quadrant of intensity data collected by θ–2θ scan technique with a variable scan rate of 4·0 to 29·3° min^{-1}, intensities of four check reflections (004,040,100,111) monitored every 100 reflections and revealed only a random variation (<2%) from their mean intensities; 1464 total reflections ($2{\cdot}5 < 2\theta < 45°$), 1377 unique reflections obtained after merging equivalent reflections ($R_{\text{int}} = 0{\cdot}045$), 1094 with $|F_o| \geq 3\sigma(|F_o|)$ used in solution and refinement of structure, data corrected for Lorentz and polarization

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* Prostaglandin E$_1$ is (11α,13E,15S)-11,15-dihydroxy-9-oxoprost-13-en-1-oic acid.

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